91602
rew 82-10

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research if
Reproduced in Whole or in Part.

ontario hydro
research division

DIFFUSION FROM CYLINDRICAL WASTE FORMS

Report No 85-127-K

G.F. Thomas
Environmental and Inorganic
Research Section
Chemical Research Department

ABSTRACT

The diffusion of a single component material from a finite cylindrical waste form, initially containing a uniform concentration of the material, is investigated. Under the condition that the cylinder is maintained in a well-stirred bath, expressions for the fractional inventory leached and the leach rate are derived with allowance for the possible permanent immobilization of the diffusant through its decay to a stable product and/or its irreversible reaction with the waste form matrix. The usefulness of the reported results in nuclear waste disposal applications is emphasized. The results reported herein are related to those previously derived at Oak Ridge National Laboratory by Bell and Nestor. A numerical scheme involving the partial decoupling of nested infinite summations and the use of rapidly converging rational approximants is recommended for the efficient implementation of the expressions derived to obtain reliable estimates of the bulk diffusion constant and the rate constant describing the diffusant-waste form interaction from laboratory data.

job	file	date	report no.
740631-528-060	837.8	May 28, 1985	85-127-K

91602
new 82-10

ontario hydro
research division

EXECUTIVE SUMMARY

DIFFUSION FROM CYLINDRICAL WASTE FORMS

G.F. Thomas
Environmental and Inorganic Research Section
Chemical Research Department

Associated with nuclear power production is the generation of potentially hazardous radioactive wastes. Prior to their long-term interim storage or permanent disposal these wastes are to be encapsulated in tailored solid waste forms. This will ensure that the wastes are immobilized for a long period of time during which their activity will be significantly reduced. Eventually the waste repository will be breached with a consequent groundwater ingress. Sound engineering practice will ensure a predictable long-term performance of a proposed repository. However, in the environmental and safety assessment of such a repository, defensible models that have been validated against field data are used to predict the long-term release and transport of radionuclides from the vault through the geosphere and to the biosphere. Both the diffusion of the encapsulated wastes through the waste form material and the integrity of the waste form with respect to corrosion determine in part the so called near-field source term, i.e., the discharge flux of radioactive material at the vault-geosphere interface. The release or source term provides a boundary condition necessary to solve the radionuclide migration models.

An early IAEA sponsored symposium on the treatment of low- and intermediate-level wastes resulted in the introduction of the first standard waste form leach test and in the formulation of its mathematical basis. Since then the general understanding of the factors affecting the leachability of nuclear waste forms has increased significantly and a variety of models have been developed to rationalize the leaching behaviors of sundry waste forms, especially glass. Most of the models are based on mass transport considerations and incorporate the Fickian diffusion of a single encapsulated material through the bulk waste form as mediated by a concentration gradient. The more sophisticated models attempt to incorporate other rate-controlling processes (such as the desorption of the diffusant at the waste form-leachant interface, redeposition of leached waste onto the solid surface, and the corrosion of the waste form), consistent with mass balance and the electroneutrality of the system. Increases in complexity ultimately lead to an analytically intractable non-linear

job	file	date	report no.
740631-528-060	837.8	May 28, 1985	85-127-K

model. A common feature of the available models is that they are one-dimensional with the waste form treated as a semi-infinite medium. A conservative criterion relating leach duration, specimen radius, and effective bulk diffusion coefficient to the degree of departure from the semi-infinite medium behavior is available.

Herein we investigate the leaching of a single component material from a finite cylindrical waste form, initially containing a uniform concentration of the material. It is assumed that diffusion through the bulk solid is the rate-controlling mechanism of the release although allowance is made for the possible permanent immobilization of the diffusant through its decay to a stable product and/or its irreversible reaction with the waste form matrix. For the worst case scenario wherein the waste form is maintained in a well-stirred leachant, expressions are derived for the fractional inventory leached and the leach rate. A numerical scheme involving the partial decoupling of nested infinite summations and the use of descending rational approximants is recommended for the efficient implementation of the expressions derived. The results reported here are related to those previously derived at Oak Ridge National Laboratory. Numerically-based algorithms that allow for the evaluation of leached inventories and leach rates of a system of encapsulated wastes are currently under development and may prove to be useful in the provision of a defensible source term model for planned Ontario Hydro nuclear waste repositories.

TABLE OF CONTENTS

	Page
1.0 INTRODUCTION	1
2.0 ANALYSIS	3
2.1 Formal Aspects	3
2.1.1 Introduction	3
2.1.2 Concentration profile	6
2.1.3 Flux through the ends	10
2.1.4 Flux through the sides	11
2.1.5 Fractional inventory leached and the leach rate	12
2.1.6 Inclusion of irreversible reaction	14
2.2 Numerical Aspects	16
2.2.1 Introduction	16
2.2.2 Computational strategies	16
3.0 DISCUSSION AND CONCLUSIONS	19
REFERENCES	25
APPENDIX	27
DISTRIBUTION LIST	last page

LIST OF FIGURES

Figure		Page
1	Cylindrical co-ordinates (ρ,z,ϕ) of an arbitrary point $\underset{\sim}{r}$ within a solid cylinder of radius a and height 2ℓ.	4
2	Contour diagram for the Bromwich integral of $c_\omega(\rho,z)$.	4
3	Contour diagram for the Bromwich integral I_m.	30

LIST OF TABLES

Table		
I	Upper bounds to the remainders (R_I) on truncation of the infinite sums $\sum_{i=1}^{\infty} x_i$ after I terms for various x's.	21

91601
new 82-10

ontario hydro
research division

To Mr. F.J. Kee
Director of Research

DIFFUSION FROM CYLINDRICAL WASTE FORMS

1.0 INTRODUCTION

Associated with nuclear power production is the generation of potentially hazardous radioactive wastes. Prior to their long-term interim storage or permanent disposal these wastes are to be encapsulated in tailored solid waste forms. This will ensure that the wastes are immobilized for a long period of time during which their activity will be significantly reduced. Eventually the waste repository will be breached with a consequent groundwater ingress. Sound engineering practice will ensure a predictable long-term performance of a proposed repository. However, in the environmental and safety assessment of such a repository, defensible models that have been validated against field data are used to predict the long-term release and transport of radionuclides from the vault through the geosphere and to the biosphere. Both the diffusion of the encapsulated wastes through the waste form material and the integrity of the waste form with respect to corrosion determine in part the so called near-field source term, i.e., the discharge flux of radioactive material at the vault-geosphere interface. The release or source term provides a boundary condition necessary to solve the radionuclide migration models.

An early IAEA sponsored symposium/1/ on the treatment of low- and intermediate-level wastes resulted in the introduction of the first standard waste form leach test/2/ and in the formulation of its mathematical basis by Bell/3/. Since then the general understanding of the factors affecting the leachability of nuclear waste forms has increased significantly/4/ and a variety of models/5-10/ have been developed to rationalize the leaching behaviors of sundry waste forms, especially glass. Most of the models are based on mass transport considerations and incorporate the Fickian diffusion of a single encapsulated material through the bulk waste form as mediated by a concentration gradient. The more sophisticated models attempt to incorporate other rate-controlling processes (such as the desorption of the diffusant at the waste form-leachant interface, redeposition of leached waste onto the solid surface, and the corrosion of the waste form), consistent with mass balance and the electroneutrality of the system. Increases in complexity ultimately lead to an analytically intractable non-linear model. A common feature of the available models is that they are one-dimensional with the waste form treated as a semi-infinite medium. Pescatore and Machiels/11/ have developed a conservative criterion relating leach duration, specimen radius, and effective bulk diffusion coefficient to the degree of departure from the semi-infinite medium behavior.

Herein we investigate the leaching of a single component material from a finite cylindrical waste form, initially containing a uniform concentration of the material. It is assumed that diffusion through the bulk solid is

the rate-controlling mechanism of the release although allowance is made for the possible permanent immobilization of the diffusant through its decay to a stable product and/or its irreversible reaction with the waste form matrix. For the worst case scenario wherein the waste form is maintained in a well-stirred leachant, expressions are derived for the fractional inventory leached and the leach rate. A numerical scheme involving the partial decoupling of nested infinite summations and the use of descending rational approximants is recommended for the efficient implementation of the expressions derived. The results reported here are related to those previously derived at Oak Ridge National Laboratory.

2.0 ANALYSIS

2.1 Formal Aspects

2.1.1 Introduction

Diffusion of the material through the cylinder is governed by the equation/12-14/

$$D\nabla^2 c(\underset{\sim}{r},t) = \frac{\partial}{\partial t} c(\underset{\sim}{r},t) \ , \qquad (2.1a)$$

where D is the diffusion constant ($m^2 \cdot s^{-1}$) and $c(\underset{\sim}{r},t)$ is the spatial ($\underset{\sim}{r}$) and temporal (t) concentration (mol/L) of the material in the cylinder, respectively. We assume that initially the cylinder contains a uniformly distributed inventory of the diffusing material, i.e.,

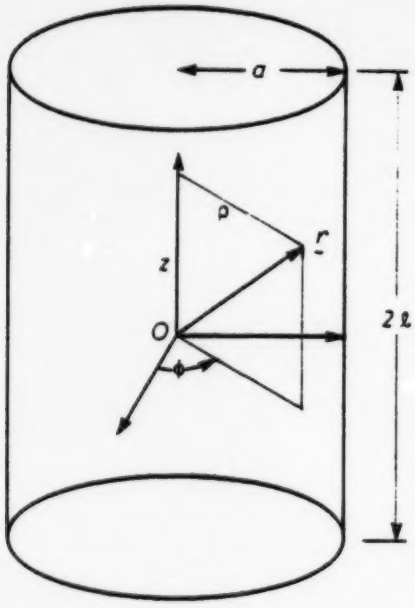

FIGURE 1

Cylindrical Co-ordinates (ρ, z, ϕ) of an Arbitrary Point $\underset{\sim}{r}$ Within A Solid Cylinder of Radius a and Height 2ℓ

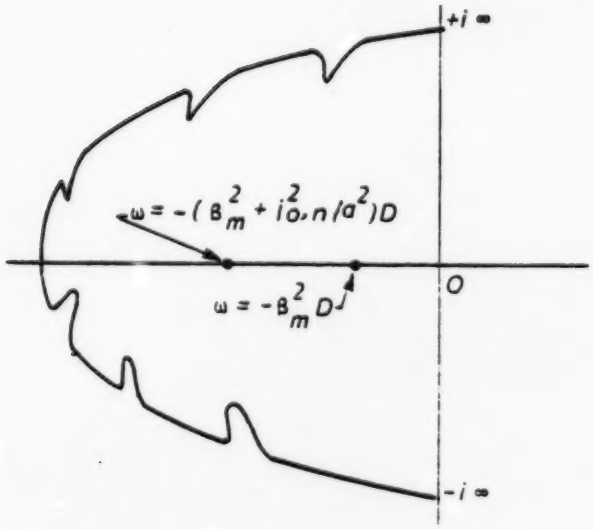

FIGURE 2

Contour Diagram for the Bromwich Integral of c_{ij} (ρ, z)

$$c(\underset{\sim}{r},0) = c_o. \tag{2.2a}$$

Referring to Fig. 1, the cylindrical co-ordinates of an arbitrary point within a cylinder of length 2ℓ and diameter $2a$ are $\underset{\sim}{r} \equiv \rho, \phi, z$, where $0 \leq \rho \leq a$, $0 \leq \phi < 2\pi$, and $|z| \leq \ell$. If the cylinder is immersed in a well-stirred tank so that the external concentration of the material is zero then the appropriate boundary conditions are

$$c(a,z,t) = 0 \tag{2.2b}$$

$$c(\rho,\pm\ell,t) = 0 \tag{2.2c}$$

for $t > 0$ and the ϕ-dependence of c has been dropped since diffusion through the cylinder is isotropic. Transforming Eq. (2.1) to ω-space gives

$$D\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{\partial^2}{\partial z^2}\right) c_\omega(\rho,z) = \omega c_\omega(\rho,z) - c_o, \tag{2.3}$$

where

$$c_\omega(\rho,z) = \int_0^\infty dt \exp(-\omega t) c(\rho,z,t) \tag{2.4a}$$

is the Laplace transform/15,16/ of $c(\rho,z,t)$. In what follows, Eq. (2.3) will be solved subject to the boundary conditions $c_\omega(a,z) = c_\omega(\rho,\pm\ell) = 0$ for $\omega > 0$ and the resultant solution $c_\omega(\rho,z)$ will be inverted to give $c(\rho,z,t)$ through explicit evaluation of the Bromwich integral

$$c(\rho,z,t) = \frac{1}{2\pi i}\int_{\alpha-i\infty}^{\alpha+i\infty} dt \exp(\omega t) c_\omega(\rho,z), \tag{2.4b}$$

where α is an arbitrary real number, using the residue theorem/16/.

2.1.2 Concentration profile

Due to the constant term on the right in Eq. (2.3), the usual separation of variables scheme is inapplicable. Assume a solution of the form

$$c_\omega(\rho,z) = \sum_{m=1}^{\infty} \alpha_m f_m(\rho)\cos\beta_m z \ , \tag{2.5}$$

where α_m and β_m are constants and $f_m(\rho)$ is a function of ρ to be determined by imposing the boundary conditions. The choice

$$\beta_m = \pi(2m-1)/2\ell \tag{2.6a}$$

ensures that $c_\omega(\rho,\pm\ell) = 0$ and substituting Eq. (2.5) into Eq. (2.3), multiplying through by $\cos\beta_n z$ and integrating over $[-\ell,+\ell]$ yields

$$\alpha_m\{-D(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}) + (\omega + \beta_m^2 D)\}f_m(\rho) = \frac{(-1)^{m-1}}{\pi(2m-1)}\ 4c_o$$

from which it follows that

$$\alpha_m = \frac{(-1)^{m-1}\ 4c_o}{\pi(2m-1)} \tag{2.6b}$$

and

$$\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right) g_m(\rho) - \mu_m^2 g_m(\rho) = 0 \ , \tag{2.7a}$$

where

$$g_m(\rho) = f_m(\rho) - 1/\mu_m^2 D \tag{2.7b}$$

and

$$\mu_m^2 = (\omega + \beta_m^2 D)/D \ . \tag{2.7c}$$

The boundary condition $c_\omega(a,z) = 0$ will be fulfilled if one takes $f_m(a) = 0$, i.e., $g_m(a) = -1/\mu_m^2 D$. With this requirement, Eq. (2.7a) has the solution

$$g_m(\rho) = - I_o(\mu_m\rho)/I_o(\mu_m a)\mu_m^2 D, \tag{2.7d}$$

where I_o is the modified Bessel function of the first kind/17,18/. Substituting Eq. (2.6b) and Eqs. (2.7b,d) into Eq. (2.5) gives

$$c_\omega(\rho,z) = \frac{2c_o}{\ell D} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{\mu_m^2\beta_m} \left\{1 - \frac{I_o(\mu_m\rho)}{I_o(\mu_m a)}\right\}\cos\beta_m z. \tag{2.8}$$

To invert Eq. (2.8) it is convenient to partition $c_\omega(\rho,z)$ into two components, viz.,

$$c_\omega^{(1)}(\rho,z) = \frac{2c_o}{\ell D} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{\mu_m^2\beta_m^2} \cos\beta_m z \tag{2.9a}$$

and

$$c_{\omega}^{(2)}(\rho,z) = \frac{2c_o}{\ell} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{\mu_m^2 \beta_m^2} \frac{I_o(\mu_m \rho)}{I_o(\mu_m a)} \cos\beta_m z, \qquad (2.9b)$$

where

$$c_{\omega}(\rho,z) = c_{\omega}^{(1)}(\rho,z) - c_{\omega}^{(2)}(\rho,z) \ . \qquad (2.9c)$$

As indicated in Fig. 2, the poles in $c_\omega(\rho,z)$ are of two types, viz., those occurring at $\omega = -\beta_m^2 D$, $m=1,2,\ldots$ and those occurring at $\omega = (\beta_m^2 + j_{o,n}^2/a^2)D, m,n=1,2,\ldots$, where J_o is a Bessel function and $J_o(j_{o,n}) = 0$, $n = 1,2,\ldots$. Since all the poles lie along the negative real axis, the contour for the Bromwich integral is conveniently taken as the imaginary axis, i.e., α is set to zero in Eq. (2.4b). The residue at the pole $\omega = -\beta_m^2 D$ is $\exp(-\beta_m^2 Dt)$ while the residue at the pole $\omega = -(\beta_m^2 + j_{o,n}^2/a^2)D$ is

$$-2\exp(-\beta_m^2 Dt) \sum_{n=1}^{\infty} \exp(-Dj_{o,n}^2 t/a^2) J_o(j_{o,n}\rho/a)/j_{o,n} J_1(j_{o,n}) \text{ for } m = 1,2,\ldots \ .$$

Application of the residue theorem/16/ yields

$$c^{(1)}(\rho,z,t) = \frac{2c_o}{\ell} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{\beta_m} \exp(-\beta_m^2 Dt)\cos\beta_m z \qquad (2.10a)$$

and

$$c^{(2)}(\rho,z,t) = c^{(1)}(\rho,z,t) \left\{1-2 \sum_{n=1}^{\infty} \frac{\exp(-j_{o,n}^2 Dt/a^2)}{j_{o,n}} \frac{J_o(j_{o,n}\rho/a)}{J_1(j_{o,n})}\right\} \ . \qquad (2.10b)$$

From Eq. (2.10) it follows that

$$c(\rho,z,t) = \frac{4c_o}{\ell} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{\beta_m} \exp(-\beta_m^2 Dt)\cos\beta_m z$$

$$\times \sum_{n=1}^{\infty} \frac{\exp(-j_{o,n}^2 Dt/a^2)}{j_{o,n}} \frac{J_o(j_{o,n}\rho/a)}{J_1(j_{o,n})} \qquad (2.11)$$

giving the variation in time of the concentration of the diffusing material as a function of the radial (ρ) and axial (z) distances. The concentration profile given in Eq. (2.11) manifestly fulfils the boundary condition $c(\rho,\pm\ell,t) = 0$ since $\cos\beta_m\ell = 0$ for all m and $c(a,z,t) = 0$ since $J_o(j_{o,n}) = 0$ for all n. Also, since/17,18(a)/

$$\sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{\beta_m} \cos\beta_m z = \frac{1}{2}\ell \text{ for } |z| < \ell \qquad (2.12a)$$

and

$$\sum_{n=1}^{\infty} \frac{J_o(j_{o,n}\rho/a)}{j_{o,n}J_1(j_{o,n})} = \frac{1}{2} \text{ for } \rho < a\ , \qquad (2.12b)$$

then clearly $c(\rho,z,o) = c_o$, the initial uniformly distributed inventory of material within the cylinder. Of course $c(\rho,z,\infty) = 0$.

2.1.3 Flux through the ends

From Eq. (2.11) the instantaneous axial flux ($mol \cdot m^{-2} \cdot s^{-1}$) towards either end of the cylinder is

$$-D\frac{\partial c}{\partial z} = \frac{4c_o D}{\ell} \sum_{m=1}^{\infty} (-1)^{m-1} \exp(-\beta_m^2 Dt) \sin\beta_m z \qquad (2.13a)$$

$$\times \sum_{n=1}^{\infty} \frac{\exp(-j_{o,n}^2 Dt/a^2)}{j_{o,n}} \frac{J_o(j_{o,n}\rho/a)}{J_1(j_{o,n})}$$

The net instantaneous flux ($mol \cdot s^{-1}$) of material through either end is

$$\int_0^{2\pi} d\phi \int_0^a d\rho\rho[-D\frac{\partial c}{\partial z}]_{z=\ell} = \frac{8\pi c_o D a^2}{\ell} \sum_{m=1}^{\infty} \exp(-\beta_m^2 Dt) \sum_{n=1}^{\infty} \frac{\exp(-j_{o,n}^2 Dt/a^2)}{j_{o,n}^2}, \qquad (2.13b)$$

where we have used the fact/17/ that

$$\int_0^a dx x J_o(bx) = (a/b) J_1(ab),$$

while the net amount (mol) of material that has diffused through either end in a time t is

$$\int_0^t dt \int_0^{2\pi} d\phi \int_0^a d\rho\,\rho \left[-D\frac{\partial c}{\partial z}\right]_{z=\ell} = \frac{8\pi c_o a^2}{\ell} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1-\exp[-(\beta_m^2+j_{o,n}^2/a^2)Dt]}{j_{o,n}^2(\beta_m^2+j_{o,n}^2/a^2)}. \quad (2.13c)$$

2.1.4 Flux through the sides

From Eq. (2.11) the instantaneous radial flux towards the wall of the cylinder is

$$-D\frac{\partial c}{\partial \rho} = \frac{4c_o D}{\ell a} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{\beta_m} \exp(-\beta_m^2 Dt)\cos\beta_m z$$

$$\times \sum_{n=1}^{\infty} \exp(-j_{o,n}^2 Dt/a^2) \frac{J_1(j_{o,n}\rho/a)}{J_1(j_{o,n})}, \quad (2.14a)$$

where the fact/18(a)/ that $J_o'(x) = -J_1(x)$ has been used. The net instantaneous flux of material through the wall is

$$\int_0^{2\pi} d\phi a \int_{-\ell}^{+\ell} dz \left[-D\frac{\partial c}{\partial \rho}\right]_{\rho=a} = \frac{16\pi c_o D}{\ell} \sum_{m=1}^{\infty} \frac{\exp(-\beta_m^2 Dt)}{\beta_m^2} \sum_{n=1}^{\infty} \exp(-j_{o,n}^2 Dt/a^2), \quad (2.14b)$$

where we have used Eq. (2.6a), while the net amount that has diffused through the wall in a time t is

$$\int_0^t dt \int_0^{2\pi} d\phi a \int_{-\ell}^{+\ell} dz \left[-D\frac{\partial c}{\partial \rho}\right]_{\rho=a} = \frac{16\pi c_o}{\ell} \sum_{m=1}^{\infty} \frac{1}{\beta_m^2} \sum_{n=1}^{\infty} \frac{1-\exp[-(\beta_m^2+j_{o,n}^2/a^2)Dt]}{\beta_m^2 + j_{o,n}^2/a^2} . \quad (2.14c)$$

2.1.5 Fractional inventory leached and the leach rate

Initially the cylinder has an inventory (mol) $2\pi a^2 \ell c_o$ of the diffusant so that at time t the fractional loss of material is given by

$$f(t) = (2\pi a^2 \ell c_o)^{-1} \{2\int_0^t dt \int_0^{2\pi} d\phi \int_0^a d\rho\rho \left[-D\frac{\partial c}{\partial z}\right]_{z=\ell} + \int_0^t dt \int_0^{2\pi} d\phi\, a \int_{-\ell}^{+\ell} dz \left[-D\frac{\partial c}{\partial \rho}\right]_{\rho=a}\} . \quad (2.15a)$$

Substituting Eqs. (2.13c) and (2.14c) into Eq. (2.15a) gives

$$f(t) = \frac{8}{\ell^2} \{ \sum_{m=1}^{\infty} \frac{1}{\beta_m^2} \sum_{n=1}^{\infty} \frac{1}{j_{o,n}^2} - \sum_{m=1}^{\infty} \frac{\exp(-\beta_m^2 Dt)}{\beta_m^2} \sum_{n=1}^{\infty} \frac{\exp(-j_{o,n}^2 Dt/a^2)}{j_{o,n}^2} \}$$

which simplifies to

$$f(t) = 1 - \frac{8}{\ell^2} \sum_{m=1}^{\infty} \frac{\exp(-\beta_m^2 Dt)}{\beta_m^2} \sum_{n=1}^{\infty} \frac{\exp(-j_{o,n}^2 Dt/a^2)}{j_{o,n}^2} \quad (2.15b)$$

on use of the identities/17,18(a)/

$$\sum_{m=1}^{\infty} \frac{1}{\beta_m^2} = \frac{1}{2}\,\ell^2 \qquad (2.16a)$$

and

$$\sum_{n=1}^{\infty} \frac{1}{j_{o,n}^2} = \frac{1}{4}\,. \qquad (12.16b)$$

Eq. (2.15b) represents the instantaneous fractional inventory leached from the cylinder so that the amount lost at time t is $2\pi a^2 \ell c_o f(t)$. Of course $f(\infty) = 1$ so that the entire inventory eventually escapes. The rate of loss ($mol \cdot s^{-1}$) of diffusant is given by

$$g(t) = \frac{16\pi c_o D a^2}{\ell} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \left(\frac{1}{a^2\beta_m^2} + \frac{1}{j_{o,n}^2}\right) \exp\left[-(\beta_m^2 + j_{o,n}^2/a^2)Dt\right], \qquad (2.17a)$$

and the leach rate ($mol \cdot m^{-2} \cdot s^{-1}$) of the diffusant from the cylinder is

$$h(t) = g(t)/[2\pi a(a + 2\ell)]\,. \qquad (2.17b)$$

Clearly $h(o) = \infty$ and $h(\infty) = 0$ so that the leach rate is initially high and eventually it vanishes.

In contrast to the foregoing approach one can remain in ω-space to evaluate f_ω which is then inverted to yield f(t); the requisite manipulations are somewhat more involved and have been relegated to the Appendix.

2.1.6 Inclusion of irreversible reaction

If the diffusant is immobilized by an irreversible reaction proceeding at a rate (s^{-1}) k then Eq. (2.1a) is modified/12-14/ to

$$D\nabla^2 c(k,\underset{\sim}{r},t) - kc(k,\underset{\sim}{r},t) = \frac{\partial}{\partial t} c(k,\underset{\sim}{r},t) \qquad (2.1b)$$

and Danckwerts/19/ has shown how to relate the solutions $c(k,\underset{\sim}{r},t)$ of Eq. (2.1b) to those $c(\underset{\sim}{r},t)$ of Eq. (2.1a) for the same initial and surface boundary conditions. The diffusion of a radioactive material of half-life $\ln 2/\lambda$ which decays to a stable product is also described by Eq. (2.1b), where $k = \lambda + k'$ and k' is the rate constant for the possible irreversible reaction of the diffusant with the bulk material.

With the initial condition $c(k,\underset{\sim}{r},o) = c_o$ and the boundary conditions $c(k,a,z,t) = c(k,\rho,\pm\ell,t) = 0$ for $t > 0$, it is trivial to show that $c(k,\rho,z,t) = \exp(-kt)c(\rho,z,t)$ is the requisite solution of Eq. (2.16). More explicitly, the concentration profile is given by

$$c(k,\rho,z,t) = \frac{4c_o}{\ell} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} (-1)^{m-1} \exp[-\{(\beta_m^2 + j_{o,n}^2/a^2)D + k\}t] \qquad (2.18)$$

$$\times \frac{J_o(j_{o,n}\rho/a)}{\beta_m j_{o,n} J_1(j_{o,n})} \cos\beta_m z.$$

2.1.6 Inclusion of irreversible reaction

If the diffusant is immobilized by an irreversible reaction proceeding at a rate (s^{-1}) k then Eq. (2.1a) is modified/12-14/ to

$$D\nabla^2 c(k,\underset{\sim}{r},t) - kc(k,\underset{\sim}{r},t) = \frac{\partial}{\partial t} c(k,\underset{\sim}{r},t) \qquad (2.1b)$$

and Danckwerts/19/ has shown how to relate the solutions $c(k,\underset{\sim}{r},t)$ of Eq. (2.1b) to those $c(\underset{\sim}{r},t)$ of Eq. (2.1a) for the same initial and surface boundary conditions. The diffusion of a radioactive material of half-life $\ln 2/\lambda$ which decays to a stable product is also described by Eq. (2.1b), where $k = \lambda + k'$ and k' is the rate constant for the possible irreversible reaction of the diffusant with the bulk material.

With the initial condition $c(k,\underset{\sim}{r},o) = c_o$ and the boundary conditions $c(k,a,z,t) = c(k,\rho,\pm\ell,t) = 0$ for $t > 0$, it is trivial to show that $c(k,\rho,z,t) = \exp(-kt)c(\rho,z,t)$ is the requisite solution of Eq. (2.16). More explicitly, the concentration profile is given by

$$c(k,\rho,z,t) = \frac{4c_o}{\ell} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} (-1)^{m-1} \exp[-\{(\beta_m^2 + j_{o,n}^2/a^2)D + k\}t]$$

$$\times \frac{J_o(j_{o,n}\rho/a)}{\beta_m j_{o,n} J_1(j_{o,n})} \cos\beta_m z. \qquad (2.18)$$

Using Eq. (2.18) and proceeding as before one obtains the analogues of Eqs. (2.13c), (2.14c), (2.15b), and (2.17a) as

$$\int_0^t dt \int_0^{2\pi} d\phi \int_0^a d\rho\rho \left[-D\frac{\partial c}{dz}\right]_{z=\ell} = \frac{8\pi c_o D a^2}{\ell} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1-\exp[-\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}t]}{j_{o,n}^2\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}}, \quad (2.19a)$$

$$\int_0^t dt \int_0^{2\pi} d\phi a \int_{-\ell}^{+\ell} dz \left[-D\frac{\partial c}{\partial \rho}\right]_{\rho=a} = \frac{16\pi c_o D}{\ell} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1-\exp[-\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}t]}{\beta_m^2\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}}, \quad (2.19b)$$

$$f(k,t) = \frac{8}{\ell^2} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{(\beta_m^2+j_{o,n}^2/a^2)D(1-\exp[-\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}t])}{\beta_m^2 j_{o,n}^2\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}}, \quad (2.19c)$$

and

$$g(k,t) = \exp(-kt)g(t), \quad (2.19d)$$

respectively. Using Eq. (2.16) in (2.19c) one obtains the net fractional inventory leached as

$$f(k,\infty) = 1 - \frac{8k}{\ell^2} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{\beta_m^2 j_{o,n}^2\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}}, \quad (2.20)$$

where the term on the extreme right is the fractional inventory that is permanently immobilized by the cylinder. Indeed one may view Eq. (2.20) as providing a description of an ideal cylindrical waste form in the sense that if k, D, a, and ℓ are such that $f(k,\infty) \approx 0$ then almost none of the waste escapes.

2.2 Numerical Aspects

2.2.1 Introduction

Particular care is required in evaluating f(k,t) as given in Eq. (2.19c). While the naive truncation of the double summation in Eq. (2.19c) may allow one to determine estimates of the parameters D and k by fitting f(k,t) to experimental data obtained on a relatively short time scale, the extension of f(k,t) to longer time scales would eventually amplify the inherent inadequacies in D and k determined in this fashion. Further, the double summation in Eq. (2.19c) converges slowly for short times. Ideally one requires a scheme for uncoupling the sums in Eq. (2.19c) and for accelerating their rates of convergence.

2.2.2 Computational strategies

Making use of Eq. (2.16) allows f(k,t) to be rewritten as

$$f(k,t) = f(k,\infty) + \exp(-kt)\,\{f(t)-1\} + \frac{8k}{\ell^2} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{\beta_m^2 j_{o,n}^2} \times \frac{\exp[-\{(\beta_m^2+j_{o,n}^2/a^2)D+k\}t]}{(\beta_m^2+j_{o,n}^2/a^2)D+k}, \tag{2.21}$$

where f(k,∞) and f(t) are given by Eqs. (2.20) and (2.15b), respectively. If the identity/18(b)/

$$\frac{\exp(-x)}{x} = \frac{1}{x} - \frac{1}{1 + \frac{1}{2}x + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!} x^{2\ell}} \tag{2.22a}$$

where the B's are Bernoulli numbers, and the identity/17/

$$\frac{1}{xy(x+y)} = \frac{2}{\pi} \int_0^{\infty} \frac{dz}{(x^2+z^2)(y^2+z^2)} \tag{2.22b}$$

are used in Eq. (2.21) one obtains

$$f(k,t) = 1 - 8k\left(\frac{D}{a\ell}\right)^2 \frac{2}{\pi} \int_0^{\infty} dz \sum_{m=1}^{\infty} \frac{(\beta_m^2 D + \frac{1}{2}k)}{\beta_m^2 D\{(\beta_m^2 D + \frac{1}{2}k)^2 + z^2\}}$$

$$\times \sum_{n=1}^{\infty} \frac{(j_{o,n}^2 D/a^2 + \frac{1}{2}k)}{j_{o,n}^2 D/a^2 \{(j_{o,n}^2 D/a^2 + \frac{1}{2}k)^2 + z^2\}}$$

$$- 8\left(\frac{Dt}{a\ell}\right)^2 \exp(-kt)\left\{\frac{\ell^2}{2Dt} - \sum_{m=1}^{\infty} \frac{1}{1 + \frac{1}{2}\beta_m^2 Dt + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!}(\beta_m^2 Dt)^{2\ell}}\right\}$$

$$\times \left\{\frac{a^2}{4Dt} - \sum_{n=1}^{\infty} \frac{1}{1 + \frac{1}{2} j_{o,n}^2 Dt/a^2 + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!}(j_{o,n}^2 Dt/a^2)^{2\ell}}\right\}$$

$$+ 8k\left(\frac{Dt}{a\ell}\right)^2 \frac{2}{\pi} \exp(-kt) \int_0^{\infty} dz \sum_{m=1}^{\infty} \left\{\frac{1}{\beta_m^2 Dt} - \frac{1}{1 + \frac{1}{2}\beta_m^2 Dt + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!}(\beta_m^2 Dt)^{2\ell}}\right\}$$

$$\times \frac{(\beta_m^2 D + \frac{1}{2}k)}{(\beta_m^2 D + \frac{1}{2}k)^2 + z^2}$$

$$x \sum_{n=1}^{\infty} \left\{ \frac{1}{j_{o,n}^2 Dt/a^2} - \frac{1}{1 + \frac{1}{2} j_{o,n}^2 Dt/a^2 + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!} (j_{o,n}^2 Dt/a^2)^{2\ell}} \right\}$$

$$x \frac{(j_{o,n}^2 D/a^2 + \frac{1}{2} k)}{(j_{o,n}^2 D/a^2 + \frac{1}{2} k)^2 + z^2} . \qquad (2.23)$$

Despite its formidable appearance, Eq. (2.23) is easy to evaluate. Use of Eq. (2.22a) essentially allows for the accelerated convergence of those terms involving summations over the B's so that these terms may be evaluated as [M,L] or [N,L] rational approximants. Use of Eq. (2.22b) allows for a partial decoupling of the double summation in Eq. (2.19c) or (2.20) and the resultant sums converge rapidly although the integral over the range (o,∞) in the dummy variable z must be evaluated by numerical quadratures; this amounts to computing the sums at a finite number N_p of Gauss-Laguerre quadrature/18(b),20/ points z_p, weighting the product of the sums by the Gauss-Laguerre weights ω_p and summing over all $p = 1,2,\ldots,N_p$.

Application of Eq. (2.22a) to Eq. (2.19d), where g(t) is given by Eq. (2.17a), gives

$$g(k,t) = \frac{16\pi c_o D^2 t}{\ell} \exp(-kt) \left[\left\{ \frac{\ell^2}{2Dt} - \sum_{m=1}^{\infty} \frac{1}{1 + \frac{1}{2} \beta_m^2 Dt + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!} (\beta_m^2 Dt)^{2\ell}} \right\} \right.$$

$$\times \sum_{n=1}^{\infty} \exp(-j_{o,n}^2 Dt/a^2)$$

$$+ \left\{ \frac{a^2}{4Dt} - \sum_{n=1}^{\infty} \frac{1}{1 + \frac{1}{2} j_{o,n}^2 Dt/a^2 + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!} (j_{o,n}^2 Dt/a^2)^{2\ell}} \right\}$$

$$\times \sum_{m=1}^{\infty} \exp(-\beta_m^2 Dt)] \qquad (2.24)$$

and again the various summations are expeditiously evaluated as [M,L] or [N,L] rational approximants.

3.0 DISCUSSION AND CONCLUSIONS

Eqs. (2.17a) and (2.19d) are identical to Eq. (19) of Bell 's report/3/. Also, Eq. (2.18) is identical to Bell's Eq. (18) provided the following typographical corrections are made: $(-1)^n$ should read $(-1)^{n-1}$, $(2n-1)^2$ should read $(2n-1)$, and π^2 should read πz. Both Eq. (2.19c) and its limiting form Eq. (2.20) appear to be new. In the event that $k = 0$, Eq. (2.19c) reduces to Eq. (2.15b), a result previously derived by Nestor/21,22/. If the diffusant is radioactive then the instantaneous activity (Ci) that has escaped from the cylinder is

$$a(t) = a_o f(k,t) \qquad (3.1a)$$

$$= \lambda \int_0^t dt\ g(k,t), \qquad (3.1b)$$

where $a_o = 2\pi a^2 \ell c_o \lambda (N_A/3.7 \times 10^{10})$ is the initial activity, N_A being Avagadro's number, and $k = \lambda + k'$ where k' is the rate constant for the possible irreversible reaction of the diffusant with the waste form matrix. Using Eq. (2.20) for $f(k,\infty)$ one obtains Bell's Eq. (20) for $a(\infty)$.

The primary advantage to be gained in adopting the scheme we have proposed for evaluating $f(k,t)$ and $g(k,t)$ is the ability to quantitatively control the errors incurred through truncation of the various infinite summations. Even though the terms appearing in the double sum in Eq. (2.19c) decrease rapidly it is not easy to obtain a priori estimates of the truncation error introduced on terminating the sums after a finite number of terms. However, use of the identity in Eq. (2.22b) decouples the double sums thus allowing for the independent control of the truncation errors. Since the remainder R_I of the infinite series $\sum_{i=1}^{\infty} a_i$ on truncation after I terms is bounded from above/20(a)/ by $\int_I^{\infty} dx\ f(x)$, where $f(x)$ is monotone decreasing for $x \geq I$ and $|a_i| \leq f(i)$ for $i \geq I$, one can determine upper limits to the remainders for the various sums appearing in Eqs. (2.23) and (2.24). The results are presented in Table I, where for summations involving the β's one uses Eq. (2.6a) and for the summations involving the j_o's one uses the fact/18(a)/ that the positive zeros of J_o lie in the interval $((n-1)\pi + 3\pi/4, (n-1)\pi + 7\pi/8)$, i.e.,

TABLE I

Upper bounds to the remainders (R_I) on truncation of the infinite sums $\sum_{i=1}^{\infty} x_i$ after I terms for various x's.

x_i	$x_i \leq$	$a_i = \beta_i^2 D$ $\quad R_I \leq$	$a_i = j_{o,i}^2 D/a^2$
$\dfrac{1}{(a_1+\frac{1}{2}k)^2 + z^2}$	$1/a_1^2$	$(\frac{2\ell}{\pi})^4 \dfrac{1}{D^2} \dfrac{1}{6(2I-1)^3}$	$(\frac{2\ell}{\pi})^4 (\frac{a^2}{D})^2 \dfrac{1}{3(I-\frac{1}{4})^3}$
$\dfrac{1}{a_1\{(a_1+\frac{1}{2}k)^2 + z^2\}}$	$1/a_1^2$	$(\frac{2\ell}{\pi})^6 \dfrac{1}{D^3} \dfrac{1}{10(2I-1)^5}$	$(\frac{2\ell}{\pi})^6 (\frac{a^2}{D})^3 \dfrac{1}{5(I-\frac{1}{4})^5}$
$\dfrac{1}{1+\frac{1}{2}a_1 t + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!} (a_1 t)^{2\ell}}$	$2/a_1 t$	$(\frac{2\ell}{\pi})^2 \dfrac{2}{Dt} \dfrac{1}{2(2I-1)}$	$(\frac{2\ell}{\pi})^2 (\frac{2a^2}{Dt}) \dfrac{1}{(I-\frac{1}{4})}$
$\dfrac{a_1 + \frac{1}{2}k}{(a_1+\frac{1}{2}k)^2 + z^2} \dfrac{1}{1 + \frac{1}{2}a_1 t + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!} (a_1 t)^{2\ell}}$	$2/a_1^2 t$	$(\frac{2\ell}{\pi})^4 \dfrac{2}{D^2 t} \dfrac{1}{6(2I-1)^3}$	$(\frac{2\ell}{\pi})^4 \dfrac{2}{t} (\frac{a^2}{D})^2 \dfrac{1}{3(I-\frac{1}{4})^3}$

$$(n-\tfrac{1}{4})\pi \leq j_{o,n} \leq (n-\tfrac{1}{8})\pi, \quad n = 1,2,.... \tag{3.2}$$

Note that in all cases the upper estimates to the R_I's are formally independent of the quadrature points $o<z<\infty$ and in the points of termination of the summations over the B's. However, since the terms in the series are rational quotients of the z's and/or the B's, they rapidly approach zero as z and/or $B_{2\ell}$ increase(s). If one has an efficient scheme for generating a sequence of Gauss-Laguerre quadrature points and weights one can readily effect a convergent estimate/20(b)/ of the integral over $o<z<\infty$. In the evaluation of g(k,t) through Eq. (2.24) one must compute the sums $\sum_{m=1}^{\infty} \exp(-\beta_m^2 Dt)$ and $\sum_{n=1}^{\infty} \exp(-j_{o,n}^2 Dt/a^2)$ which converge slowly for $Dt \ll \ell^2$ and $Dt \ll a^2$, respectively and formally diverage when t = 0. If for the infinite series $\sum_{i=1}^{\infty} x_i$, $\left|x_{i+1}/x_i\right| \leq k < 1$ for all $i \geq I$ then/20(a)/ $R_I \leq (k/1-k)\left|x_I\right| \leq (k/1-k)$ if $\left|x_I\right| \leq 1$. Using Eq. (2.6a) one can show that a suitable k for the sum over the β's is $k = \exp(-2\pi^2 Dt/\ell^2)$ and using Eq. (3.2) one can show that a suitable k for the sum over the j_o's is $k = \exp(-35Dt/64a^2)$. However, if $Dt \ll \ell^2$ then one should apply Eq. (2.22a) and evaluate the sum over the β's as

$$\sum_{m=1}^{\infty} \exp(-\beta_m^2 Dt) = \sum_{m=1}^{\infty} \left\{1 - \frac{\beta_m^2 Dt}{1 + \frac{1}{2}\beta_m^2 Dt + \sum_{\ell=1}^{\infty} \frac{B_{2\ell}}{(2\ell)!}(\beta_m^2 Dt)^{2\ell}}\right\}$$

and similarly for the sum over the j_o's when $Dt \ll a^2$. Nester/21/ has developed a scheme for expediting the evaluation of f(t) as given in

Eq. (2.15b). The procedure is based on the asymptotic properties of Bessel functions and the use of rational approximants but no truncation error estimates are provided.

Both Bell/3/ and Nestor/21/ have considered the applicability of the infinite medium behavior to leaching from a finite cylindrical test specimen while Pescatore and Machiels/14/ have given a conservative criterion relating leach duration, specimen radius, and effective bulk diffusion coefficient to the degree of departure of spherical and cylindrical volumetric configurations from semi-infinite medium behavior. Recent results/23/ of a laboratory evaluation of a near-field repository performance assessment model/24/ indicated that the agreement between the model and the experimental simulations was good at relatively high flow rates. The model was one-dimensional and the specimens were cylindrical in shape but by using a sufficiently large test chamber, wall effects were minimized. Machiels/25/ has given an interesting treatment of the leaching of ^{90}Sr from hemispherical aluminosilicate glass waste forms buried at the Chalk River Nuclear Laboratories in shallow soil without a canister, backfill, or other barriers. A finite geometry model/9(a)/ was used and in order to obtain good agreement with the data (which was available over a 15 year period) one had to describe the release process by either two diffusion constants or by diffusion and an initial surface release term. Whatever the mechanism of release, the leach rate decreases exponentially, not at all unlike the $t^{-1/2}$-type behavior exhibited by a semi-infinite medium model. Numerically-based algorithms that allow for the evaluation

of leached inventories and leach rates of a system of encapsulated wastes are currently under development/26/ and may prove to be useful in the provision of a defensible source term model for planned Ontario Hydro nuclear waste repositories.

Approved:

O.A. Kupcis
Manager
Chemical Research Dept

Prepared by:

G.F. Thomas
Chemist
Environmental and Inorganic
Research Section

Reviewed by:

D.J. Dodd
Supervising Enginer
Environmental and Inorganic
Research Section

GFT:db/km

REFERENCES

1. Treatment of Low- and Intermediate-Level Radioactive Waste Concentrates, Technical Report Series No. 82, International Atomic Energy Agency, Vienna, 1968.

2. E.D. Hespe, "Leach Testing of Immobilized Radioactive Waste Solids. A Proposal for Standard Method". At. Energy Rev. 9, 195-207 (1971).

3. M.J. Bell, "An Analysis of the Diffusion of Radioactivity from Encapsulated Wastes", ORNL-TM-3232, February 1971.

4. Special Issue: Leachability of Radioactive Solids. C.E. Bamberger et al., eds., Nucl. Chem. Waste Manag. 2, no. 2 (1981).

5. H.W. Godbee and D.S. Joy, "Assessment of the Loss of Radioactive Isotopes from Waste Solids to the Environment. Part I: Background and Theory, "ORNL-TM-4333, February 1974.

6. (a) J.G. Moore, H.W. Godbee, and A.H. Kibbey, "Leach Behavior of Hydrofracture Grout Incorporating Radioactive Wastes", Nucl. Technol. 32, 39-52 (1977); (b) H.W. Godbee et al., "Applications of Mass Transport Theory to the Leaching of Radionuclides from Solid Wastes", Nucl. Chem. Waste Manag. 1, 29-35 (1980).

7. O.U. Anders, J.F. Bartel, and S.J. Altschuler, "Determination of the Leachability of Solids", Anal. Chem. 50, 564-569 (1978).

8. J.R. Wiley, "Leach Rates of High Activity from Borosilicate Glass", Nucl. Technol. 43, 268-272 (1979).

9. (a) C. Pescatore and A.J. Machiels, "Modeling of Glass Leaching", Trans. Am. Nucl. Soc. 33, 416-417 (1979); (b) "Effects of Surfaces on Glass Waste Form Leaching", presented at the Sixth University Conference on Glass Science; Glass Microstructure: Surface and Bulk, July 29-31, 1981, The Pensylvania State University; (c) "Effects of Surfaces on Glass Waste Form Leaching", J. Non-Cryst. Solids 49, 379 (1982); (d) A.J. Machiels and C. Pescatore, "The Influence of Surface Processes in Waste Form Leaching", in Scientific Basis for Nuclear Waste Management, Vol. 3, pp 371-378, J.G. Moore ed. (Plenum Press, New York, 1981).

10. P.J. Melling and A.R. Allnatt, "Modeling of Leaching and Corrosion of Glass", J. Non-Cryst. Solids 42, 553-560 (1980).

11. C.S. Pescatore and A.J. Machiels, "A Criterion for Selecting Leach Test Specimen Sizes", Nucl. Technol. 56, 297-301 (1982).

12. H.S. Carslaw and J.C. Jaeger, Conduction of Heat in Solids (Clarendon Press, Oxford, 1959).

13. J. Crank, The Mathematics of Diffusion (Clarendon Press, Oxford, 1964).

14. W. Jost, Diffusion in Solids, Liquids, and Gases (Academic Press, New York, 1965).

15. H.S. Carslaw and J.C. Jaeger, Operational Methods in Applied Mathematics (Oxford University Press, Oxford, 1949).

16. N.W. McLachlan, Complex Variable and Operational Calculus With Technical Applications (Cambridge University Press, Cambridge, 1939).

17. I.S. Gradshteyn and I.M. Ryzhik, Table of Integrals, Series, and Products (Academic Press, New York, 1965).

18. (a) G.N. Watson, A Treatise on the Theory of Bessel Functions (Cambridge University Press, Cambridge, 1952);

(b) Handbook of Mathematical Functions, M. Abramowitz and J.A. Stegun, eds. (Dover, New York, 1972).

19. P.V. Danckwerts, "Absorption by Simultaneous Diffusion and Chemical Reaction into Particles of Various Shapes and Into Falling Drops", Trans. Faraday Soc. 47, 1014-1023 (1951).

20. (a) G. Dahlquist and A. Bjorck, Numerical Methods (Prentice-Hall, Englewood Cliffs, New Jersey, 1974);

(b) A. Ralston, A First Course in Numerical Analysis (McGraw-Hill, New York, 1965).

21. C.W. Nestor, "Diffusion From Solid Cylinders", ORNL/CSD/TM-84, January 1980.

22. Note that the assumption made in Ref. 21 that $c_\omega(\rho,z)$ is separable is invalid. However, the expression derived for f(t) is valid. C.W. Nestor, Jr., private communication, 1984.

23. B.P. McGrail, L.A. Chick, and G.L. McVay, "Initial Results for the Experimental Evaluation of a Nuclear Waste Repository Source Term Model", Nucl. Technol. 69, 114-118 (1985).

24. P.L. Chambre et al., "Analytical Performance Models for Geologic Repositories", LBL-1482, Vol. II, 1982.

25. A.J. Machiels, "Short-term Leaching Behavior of Waste Forms. A Potential Area for Improvement", presented at the Workshop on Alternate Nuclear Waste Forms and Interactions in Geologic Media, Gatlinburg, TN, May 13-15, 1980, DOE-CONF-8005108, April 1981.

26. G.F. Thomas, work in progress.

APPENDIX

From Eq. (2.15a) one has

$$f(t) = \int_0^t dt F(t), \tag{A.1a}$$

where

$$F(t) = (2\pi a^2 \ell c_o)^{-1} \left\{ 2 \int_0^{2\pi} d\phi \int_0^a d\rho\rho \left[-D \frac{\partial c}{\partial z} \right]_{z=\ell} + \int_0^{2\pi} d\phi a \int_{-\ell}^{+\ell} dz \left[-D \frac{\partial c}{\partial \rho} \right]_{\rho=a} \right\}. \tag{A.1b}$$

In ω-space, $f_\omega = \frac{1}{\omega} F_\omega$. Starting with Eq. (2.8) one obtains for the axial flux in ω-space

$$(2\pi a^2 \ell c_o)^{-1} \, 2 \int_0^{2\pi} d\phi \int_0^a d\rho\rho \left[-D \frac{\partial c_\omega}{dz} \right]_{z=\ell} = \frac{2}{\ell^2} \sum_{m=1}^{\infty} \frac{1}{\mu_m^2} \left\{ 1 - 2 \frac{I_1(\mu_m a)}{\mu_m a \, I_o(\mu_m a)} \right\} \tag{A.2a}$$

and for the radial flux,

$$(2\pi a^2 \ell c_o)^{-1} \int_0^{2\pi} d\phi a \int_{-\ell}^{+\ell} dz \left[-D \frac{\partial c_\omega}{\partial \rho} \right]_{\rho=a} = \frac{4}{\ell^2} \sum_{m=1}^{\infty} \frac{1}{\beta_m^2} \frac{I_1(\mu_m a)}{\mu_m a \, I_o(\mu_m a)} . \tag{A.2b}$$

Combining Eqs. (A.2a) and (A.2b) and using Eq. (2.7c) one obtains

$$F_\omega = \frac{2}{\ell^2} \sum_{m=1}^{\infty} \frac{1}{\mu_m^2} \left\{ 1 + \frac{2\omega}{D\beta_m^2 \mu_m a} \frac{I_1(\mu_m a)}{I_o(\mu_m a)} \right\} \tag{A.3a}$$

and so

$$f_\omega = \frac{2}{\ell^2} \sum_{m=1}^{\infty} \frac{1}{\omega\mu_m^2} + \frac{4a^2}{\ell^2 D} \sum_{m=1}^{\infty} \frac{1}{\beta_m^2} \frac{I_1(\mu_m a)}{(\mu_m a)^3 I_o(\mu_m a)} . \qquad (A.3b)$$

We are now required to invert Eq. (A.3b) to obtain

$$f(t) = \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} d\omega \exp(\omega t) f_\omega . \qquad (A.4)$$

Substituting Eq. (A.3b) into Eq. (A.4), applying the residue theorem/16/, and making use of Eq. (2.16a) one can easily show that

$$f(t) = 1 + \frac{2}{\ell^2} \sum_{m=1}^{\infty} (2 I_m - 1) \frac{\exp(-\beta_m^2 Dt)}{\beta_m^2} , \qquad (A.5a)$$

where the Bromwich integral I_m is given by

$$I_m = \frac{1}{2\pi i} \int_{\alpha-i\infty}^{\alpha+i\infty} d\omega \frac{\exp[(\omega + \beta_m^2 D)t] \; I_1[D^{-1/2} a(\omega + \beta_m^2 D)^{1/2}]}{D^{-1/2} a(\omega + \beta_m^2 D)^{3/2} \; I_o[D^{-1/2} a(\omega + \beta_m^2 D)^{1/2}]} .$$

Setting $u = \omega + \beta_m^2 D$ and $v = D^{-1/2} a$,

$$I_m = \frac{1}{2\pi i} \int_{Br_1} du \frac{\exp(ut) I_1(vu^{1/2})}{vu^{3/2} \; I_o(vu^{1/2})}$$

and the contour Br_1 is displayed in Fig. 3. On Br_1, $u = \alpha + iy$. Put $u = s^2$, i.e., $s = (\alpha^2 + y^2)^{1/4} \exp(i\phi/2)$ where $\phi = \tan^{-1}(y/\alpha)$. When $y = 0$, Br_1 crosses the real axis and so $\phi = 0$ and $s = \alpha^{1/2}$. The representative point in the s-plane falls either to the left or right of Br_1 according as $\alpha>1$ or $\alpha<1$. When $y = \pm\infty$, $\phi = \pm \pi/2$ and so $s \sim y^{1/2}\exp(\pm i\pi/4)$ and the contour Br_3 in the s-plane is asymptotic to the lines $y^{1/2} \times \exp(\pm i\pi/4)$. If one writes $s = p + iq$ then $p^2 - q^2 =$ constant and the contour is a hyperbola. Rather than use this contour it is convenient to find an equivalent path to facilitate the integration. If the imaginary axis indented on the right at the origin 0 is used as contour, on the small semi-circle $s = \varepsilon \exp(i\theta)$ where $|\theta| \leq \pi/2$ and so the contribution $I_m^{(1)}$ from the pole at the origin is

$$I_m^{(1)} = \lim_{\varepsilon\to 0} \frac{2}{v} \frac{1}{2\pi i} \int_{-\pi/2}^{\pi/2} d\theta \, \frac{\exp[\varepsilon^2 \exp(i2\theta)] \; i\,\varepsilon \exp(i\theta) I_1[v\varepsilon \exp(i\theta)]}{\varepsilon^2 \exp(i2\theta)\, I_0[v\varepsilon \exp(i\theta)]} ,$$

$$= \frac{1}{v\pi} \int_{-\pi/2}^{\pi/2} d\theta \exp(-i\theta) \lim_{\varepsilon\to 0} \{\varepsilon^{-1} I_1[v\varepsilon \exp(i\theta)]\} .$$

Since $\lim_{\varepsilon\to 0} \{\varepsilon^{-1} I_1 [v\varepsilon \exp(i\theta)]\} = \frac{1}{2} v \exp(i\theta)$ it follows that

$$I_m^{(1)} = \frac{1}{2} . \qquad \text{(A.5b)}$$

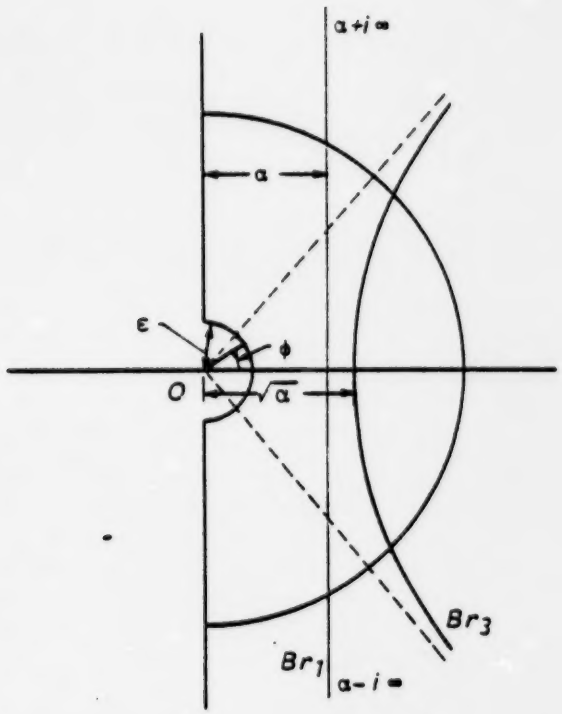

FIGURE 3

Contour Diagram for Evaluating the Bromwich Integral I_m

On the imaginary axis, $s = iy$ and so

$$I_m^{(2)} = \lim_{\varepsilon \to 0} \frac{1}{2\pi i} \frac{2}{v} \left\{ \int_{-\infty}^{-\varepsilon} dy \, \frac{\exp(-y^2 t) I_1(ivy)}{y^2 I_o(ivy)} + \int_{\varepsilon}^{\infty} dy \, \frac{\exp(-y^2 t) I_1(ivy)}{y^2 I_o(ivy)} \right\}$$

$$= -\frac{1}{v\pi} \int_{-\infty}^{\infty} dy \, \frac{\exp(-y^2 t) I_1(ivy)}{y^2 I_o(ivy)} .$$

To evaluate this integral we select a contour to isolate the pole at the origin and since/18/ $I_o(x) = J_o(ix)$ we calculate the residue at $y = j_{o,n}/v$ to be

$$\frac{\exp(-j_{o,n}^2 t/v^2)\ I_1(ij_{o,n})}{j_{o,n}^2/v^2 \frac{d}{dy} \{I_o(ivy)\}_{y=j_{o,n}/v}} = -iv \frac{\exp(-j_{o,n}^2 t/v^2)}{j_{o,n}^2}.$$

Applying the residue theorem one obtains

$$I_m^{(2)} = -2 \sum_{n=1}^{\infty} \frac{\exp(-j_{o,n}^2 Dt/a^2)}{j_{o,n}^2} , \qquad \text{(A.5c)}$$

where we have reset $v = D^{-1/2} a$. Combining Eqs. (A.5b) and (A.5c) to yield I_m (which turns out to be independent of the index m) and substituting into Eq. (A.5a) gives Eq. (2.15b).